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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : D01F 2/00

A1

(11) International Publication Number: WO 98/02602

(43) International Publication Date: 22 January 1998 (22.01.98)

(21) International Application Number: PCT/GB97/01882

(22) International Filing Date: 11 July 1997 (11.07.97)

(30) Priority Data:
9614679.0 12 July 1996 (12.07.96) GB

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(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: METHOD FOR THE MANUFACTURE OF LYOCELL FIBRE

(57) Abstract

Control over the fibrillation tendency of lyocell fibres can be obtained by applying an aqueous solution of an alkali metal hydroxide to the fibre in never-dried state under conditions such that the lengthwise shrinkage of the fibre during this step is controlled at a value within the range from 5 to 20 percent.

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METHOD FOR THE MANUFACTURE OF LYOCELL FIBRE

Field of the invention

This invention relates to processes for the manufacture of lyocell fibre which include the step of contacting the fibre in never-dried state with an aqueous solution of an alkali metal hydroxide.

Lyocell fibres are known, and their manufacture is described for example in US-A-4,416,698, the contents of which are incorporated herein by way of reference. Cellulose is dissolved in a solvent containing a tertiary amine N-oxide (which may also be called for brevity an amine oxide), for example N-methylmorpholine N-oxide (NMMO). The solvent generally also contains a proportion of a non-solvent for cellulose, for example water. The resulting solution is extruded through a suitable die to produce fibres, which are coagulated, washed in water to remove the solvent, and dried. This process of extrusion and coagulation is referred to as "solvent spinning", and the cellulose fibre produced thereby is referred to as "solvent-spun" cellulose fibre or as lyocell fibre. It is also known that cellulose fibres can be made by extrusion of a solution of a cellulose derivative into a coagulating and regenerating bath. One example of such a process is the viscose process, in which the cellulose derivative is cellulose xanthate. Solvent spinning has a number of advantages over other known processes for the manufacture of elongate cellulose members, such as the viscose process, for example reduced environmental emissions.

Lyocell fibres are known to be prone to fibrillation. Fibrillation is a phenomenon which in the main occurs when lyocell fibres are subjected to mechanical forces during wet-processing, and it results in the partial detachment of fine longitudinal fibrils from the fibres. Fibrillation is in general considered to be undesirable in textile end-uses, and efforts have been made to reduce or eliminate

fibrillation tendency by chemical aftertreatments, such as those described in US-A-5,310,424, or by suitable choice of spinning parameters, as described for example in WO-A-95/02082.

International Patent Application PCT/GB96/03160 (published as WO97/23668) describes a process for the manufacture of an extruded lyocell article such as fibre which includes the characterising step of applying to the reconstituted but never-dried lyocell article an aqueous solution of an alkali metal hydroxide containing from 0.20 to 3.85 percent by weight hydroxide ions. An aqueous solution containing from 0.5 to 9 percent by weight sodium hydroxide may be used. The aqueous solution of alkali metal hydroxide may conveniently be applied to the fibre from a circulating bath, the residence time of the reconstituted article therein conveniently being in the range from 20 to 90 seconds. This process is said to enable the manufacture of lyocell articles having increased dyeability, increased whiteness, reduced yellowness and/or increased absorbency.

Copending unpublished British patent application no. 9611252.9 describes a process for the manufacture of lyocell fibre which includes the characterising step of applying to the reconstituted but never-dried fibre for 20 seconds or more an aqueous liquor which comprises from 10 to 18 percent by weight sodium hydroxide. This process is said to enable the manufacture of lyocell fibre with controlled, in particular reduced, fibrillation tendency.

It is known that cellulose exhibits a swelling maximum in aqueous sodium hydroxide at a sodium hydroxide concentration of about 10 percent by weight. The present inventors have found that lyocell fibres may tend to shrink in length during treatment in relaxed state with sodium hydroxide, in particular at and around the swelling maximum, and that excessive shrinkage has adverse effects on the tensile properties of the fibres. It is an object of the

present invention to provide a method of avoiding such adverse effects on the tensile properties, while retaining the benefits of sodium hydroxide treatment.

Disclosure of the invention

Under the present invention lyocell fibre is manufactured by a method which includes the step of contacting the fibre in never-dried state with an aqueous solution of an alkali metal hydroxide, and the lengthwise shrinkage of the fibre during the said step is controlled at a value within the range from 5 to 20 percent.

According to the invention there is provided a method for the manufacture of lyocell fibre, including the steps in sequential order of:

(1) extruding a solution of cellulose in an organic solvent through a die, thereby producing an elongate form;

(2) passing the elongate form through at least one water-containing bath to remove the organic solvent from the elongate form, thereby producing never-dried lyocell fibre;

(3) applying to the never-dried lyocell fibre an aqueous solution of an alkali metal hydroxide;

(4) washing the never-dried lyocell fibre to remove alkali metal hydroxide therefrom; and

(5) drying the never-dried lyocell fibre, thereby forming the lyocell fibre,

characterised in that the lengthwise shrinkage of the never-dried lyocell fibre during step (3) is controlled at a value in the range from 5 to 20 percent.

The fibre is dried for the first time in step (5). The organic solvent is preferably a tertiary amine N-oxide, further preferably N-methylmorpholine N-oxide, and preferably contains a minor proportion of water. The solution preferably comprises from 5 to 30, more preferably from 15 to 25, percent by weight cellulose and from 5 to 20 percent by weight water. The solution may additionally comprise one or more other substances, for example a thermal stabiliser such as propyl gallate, in known manner.

The titre of the lyocell fibre may be in the range from 0.5 to 10 decitex.

In a first embodiment, the method of the invention is performed on lyocell fibre in the form of continuous filament yarn or tow and the lengthwise shrinkage of the fibre during the alkali treatment step is controlled by controlling the ratio of the velocities of the fibre as it leaves and enters the said step to be within the range from 0.8:1 to 0.95:1.

In a second embodiment, the method of the invention may be performed on lyocell fibre in the form of continuous filament yarn, tow or staple fibre and the lengthwise shrinkage of the fibre during the alkali treatment step is controlled by suitable choice of the concentration of alkali metal hydroxide and the temperature of the aqueous solution. In this embodiment, the lengthwise shrinkage of the fibre is conveniently measured by treating a sample of never-dried fibre cut to known length, for example 25 cm long, in relaxed state with the aqueous solution, followed by washing and drying, and comparing the length of the dried fibre with that of the cut fibre prior to the alkali treatment step.

The alkali metal hydroxide is preferably sodium hydroxide, although other compounds such as potassium hydroxide may alternatively be used. The aqueous solution of alkali metal hydroxide may comprise from 5 to 18, preferably

from 8 to 13, percent by weight sodium hydroxide. The temperature of the aqueous solution of alkali metal hydroxide is preferably in the range from 0 to 60°C, more preferably from 20 to 30 °C. It will be appreciated that routine experimentation may be required in the second embodiment of the invention to select conditions of concentration and temperature which ensure that the lengthwise shrinkage of the fibre falls within the desired range.

The aqueous solution of alkali metal hydroxide may be applied to the fibre by any convenient conventional means, for example using a circulating bath, wicking roller or spray. When a circulating bath is used, the residence time of the fibre therein may conveniently be in the range from 5 to 120 seconds.

After the alkali treatment step, alkali metal hydroxide is washed from the fibre. In one embodiment of the invention, the fibre is washed with hot water, preferably followed by a sour wash with dilute aqueous acid so that the fibre pH is below 7. In another embodiment of the invention, the fibre is washed with an aqueous acid solution. The acid may be a mineral acid such as hydrochloric acid or sulphuric acid, the concentration thereof in the aqueous acid solution being in the range from 0.1 to 20, preferably from 1 to 15, percent by volume, or it may be an organic acid such as acetic acid, the concentration thereof in the aqueous acid solution being in the range from 25 to 75, preferably from 40 to 60, percent by volume. The washing liquor may be applied to the fibre by any convenient means, for example using a circulating bath, wicking roller or spray. When an aqueous acid solution is used, the residence time of the fibre in such a circulating bath may conveniently be in the range from 5 to 120 seconds.

The method of the invention has the advantage that it permits control over and maintenance of fibre tensile

properties at the same time as it imparts the advantages which flow from treatment of never-dried lyocell fibres with aqueous alkali as described in the aforementioned British patent applications.

Test Method 1

Dry lyocell fibre (approx 0.05 g) is cut to 10 mm lengths and placed in an industrial blender together with 400 ml tap The blender is then operated for a time between 30 second and 3 minutes to induce fibrillation; the time required depends inter alia on the nature of the blender blade and is chosen so that a standard sample of commercial lyocell fibre (available from Courtaulds Fibres (Holdings) Limited under the Trade Mark TENCEL) exhibits a fibrillation index in the range 6.5 to 8.0. The fibre is then collected and dried and assessed for degree of fibrillation.

There is no universally accepted standard for assessment of fibrillation, and the following method was used to assess Fibrillation Index (F.I.). A series of samples of fibre having nil and increasing degrees of fibrillation was identified. A standard length of fibre from each sample was then measured, and the number of fibrils (fine hairy spurs extending from the main body of the fibre) along the standard length was counted. The length of each fibril was measured, and an arbitrary number, being the product of the number of fibrils multiplied by the average length of each fibril, was determined for each fibre. The fibre exhibiting the highest value of this product was identified as being the most fibrillated fibre and was assigned an arbitrary Fibrillation Index of 10. The wholly unfibrillated fibre was assigned a Fibrillation Index of zero, and the remaining fibres were graded from 0 to 10 based on the microscopically measured arbitrary numbers.

The measured fibres were then used to form a standard graded scale. To determine the Fibrillation Index for any

other sample of fibre, five or ten fibres were visually compared under the microscope with the standard graded fibres. The visually determined numbers for each fibre were then averaged to give a Fibrillation Index for the sample under test. It will be appreciated that visual determination and averaging is many times quicker than measurement, and it has been found that skilled fibre technologists are consistent in their rating of fibres.

In general, fabrics containing fibre with F.I. 2 or more may have a "frosted" appearance. A desirable target for fibre F.I. is 1 or less, preferably 0.5 or less, in fabric, including laundered fabric.

The invention is illustrated by the following Examples, in which parts and proportions are by weight unless otherwise specified.

Example 1

A solution of cellulose (15%) in NMMO (75%) and water (10%) was extruded through a spinnerette into an aqueous coagulating bath to produce 1.7 dtex filaments. After washing with water to remove NMMO, the filaments were treated in relaxed state with an aqueous solution of sodium hydroxide for 30 seconds, washed with 15% v/v aqueous sulphuric acid solution for 30 seconds, rinsed and dried. Further experimental details and results are given in Table 1:

Table 1

Treatment conditions	Shrinkage %	Tenacity cN/tex	Extension %	F.I.
Untreated control	2	ca. 40	ca. 15	6-7
5% NaOH/20°C (1)	2	36.1	16.0	6.3
6% NaOH/20°C (1)	3	36.2	17.7	4.4
7% NaOH/20°C	6	32.4	18.6	4.4
15% NaOH/60°C	6	36.3	17.4	1.7
18% NaOH/60°C	6	37.0	18.3	1.6
13% NaOH/30°C	10	30.8	19.2	1.9
18% NaOH/20°C	10	31.2	17.8	0.8
8% NaOH/20°C	12	31.8	19.3	2.7
15% NaOH/20°C	12	29.7	19.3	1.0
11% NaOH/25°C	14	29.1	13.7	2.1
13% NaOH/20°C	16	28.3	19.7	3.1
11% NaOH/20°C	20	24.6	19.9	3.2
8% NaOH/15°C (1)	26	24.0	17.9	1.6

(1) Comparative experiment.

In other comparative experiments, fibre was treated with 9-13% NaOH solutions at 10°C, shrinkage being measured at around 40%; or with 9 or 11% NaOH solutions at 5°C, shrinkage being measured at around 50%. In every case, the fibres were severely weakened, and F.I.s were unmeasureable because the fibres disintegrated during testing.

Example 2

Lyocell fibre was spun and washed as in Example 1. The fibre in tow form was then passed first through a bath containing 11% w/v aqueous sodium hydroxide at 25°C and next through a bath containing 15% v/v aqueous sulphuric acid at ambient temperature, either under tension or in relaxed state. In the experiment conducted under tension, roller speeds into and out of the NaOH bath were

2.69 and 2.16 m/min respectively, corresponding to a controlled shrinkage of 19.3%. The fibre was then rinsed and dried as in Example 1. The results shown in Table 2 were obtained:

Table 2

	Tenacity cN/tex	Extension %	F.I.
Untreated control		ca.40	ca.156-7
Under tension	35.0	13.8	3.2
Relaxed	31.3	17.9	2.4

The fibre treated under tension exhibited a good combination of properties in comparison with that treated in relaxed state, and both samples exhibited a good combination of properties in comparison with the control.

CLAIMS

1. A method for the manufacture of lyocell fibre, including the steps in sequential order of:

(1) extruding a solution of cellulose in an organic solvent through a die, thereby producing an elongate form;

(2) passing the elongate form through at least one water-containing bath to remove the organic solvent from the elongate form, thereby producing never-dried lyocell fibre;

(3) applying to the never-dried lyocell fibre an aqueous solution of an alkali metal hydroxide;

(4) washing the never-dried lyocell fibre to remove alkali metal hydroxide therefrom; and

(5) drying the never-dried lyocell fibre, thereby forming the lyocell fibre,

characterised in that the langthwise shrinkage of the never-dried cellulose during step (3) is controlled at a value within the range from 5 top 20 percent.

2. A method according to claim 1, further characterised in that the organic solvent is aqueous N-methylmorpholine N-oxide.

3. A method according to claim 1 or claim 2, further characterised in that the alkali metal hydroxide is sodium hydroxide.

4. A method according to claim 3, further characterised in that the concentration of sodium hydroxide in the aqueous solution is in the range from 5 to 18 percent by weight, preferably in the range from 8 to 13 percent by weight.

5. A method according to any one of the preceding claims, further characterised in that the temperature of the aqueous solution is in the range from 0.60°C, preferably in

the range from 20 to 30°C.

6. A method according to any one of the preceding claims, further characterised in that washing step (4) involves washing firstly with hot water and secondly with dilute aqueous acid, whereby the pH of the lyocell fibre is below 7.

7. A method according to any one of claims 1 to 5, further characterised in that washing step (4) involves washing with an aqueous solution containing from 0.1 to 20 percent by volume, preferably from 1 to 15 percent by volume, of an acid selected from the group consisting of hydrochloric acid and sulphuric acid.

8. A method according to any one of claims 1 to 5, further characterised in that washing step (4) involves washing with an aqueous solution containing from 25 to 75 percent by volume, preferably from 40 to 60 percent by volume, acetic acid.

9. A method according to any one of the preceding claims, further characterised in that the never-dried fibre in step (3) is in the form of yarn or tow and in that the ratio of the velocities of the fibre as it leaves and enter step (3) is controlled to be in the range from 0.8:1 to 0.95:1.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 97/01882

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 D01F2/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 D01F C08J D06M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,A	WO 97 23668 A (COURTAULDS FIBRES) 3 July 1997 cited in the application ---	
A	WO 95 24524 A (COURTAULDS FIBRES HOLDINGS LTD ;TAYLOR JAMES MARTIN (GB)) 14 September 1995 see the whole document ---	
A	WO 95 28516 A (COURTAULDS FIBRES HOLDINGS LTD ;POTTER CHRISTOPHER DAVID (GB); DOB) 26 October 1995 see the whole document ---	
A	WO 92 14871 A (COURTAULDS PLC) 3 September 1992 see the whole document -----	

☐ Further documents are listed in the continuation of box C

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
7 November 1997	13. 11. 97

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/GB 97/01882

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